Atomic Layer Deposition of Alumina on Zirconia, Ceria, and Titania

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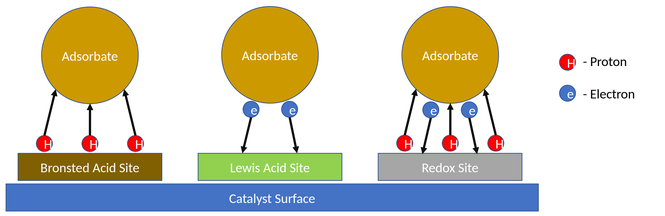
Background and Motivation

- Although widely used in industry, metal oxides are difficult to study and tune due to surface heterogeneity, due to a multitude of active sites and surface defects.

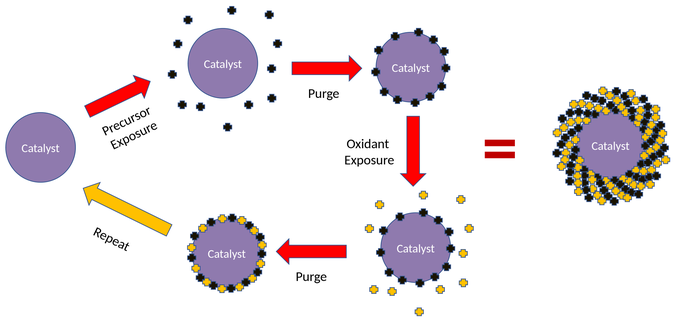


- Because many processes use catalysts, highly efficient catalysts can reduce waste, energy costs, and time required to run a reaction.
- Understanding how changing the expression of active sites affects catalyst properties and harnessing these effects can enhance sustainability across industries.

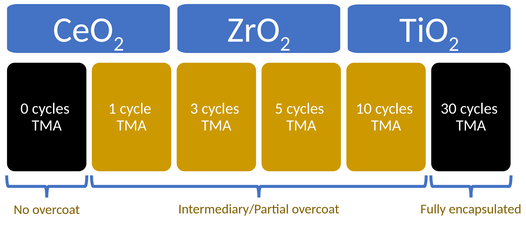
How can metal oxide catalysts be tailored to exhibit specific properties?

Synthesis – Atomic Layer Deposition

- Overcoating enables tuning of catalyst properties, but to apply this technique advantageously, subtle effects at the surface level must be well documented.



- Using atomic layer deposition (ALD) to apply atomically precise layers of a secondary substance to a catalyst, this study recorded the changes in surface chemistry when partial overcoats of alumina (TMA) were applied to zirconia, ceria, and titania.

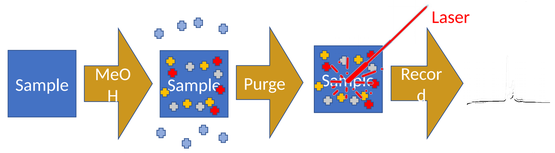


- ALD can affect reaction channels by altering reaction variables such as binding energy, adsorption strength, and interfaces. Overcoating by ALD also enhances the durability of catalysts under severe reaction conditions.

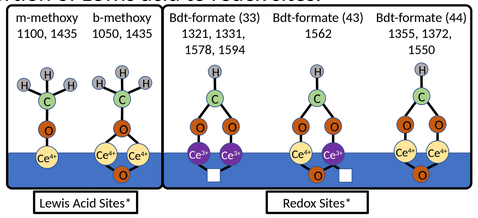
Characterization – Methanol DRIFTS (MeOH-DRIFTS)

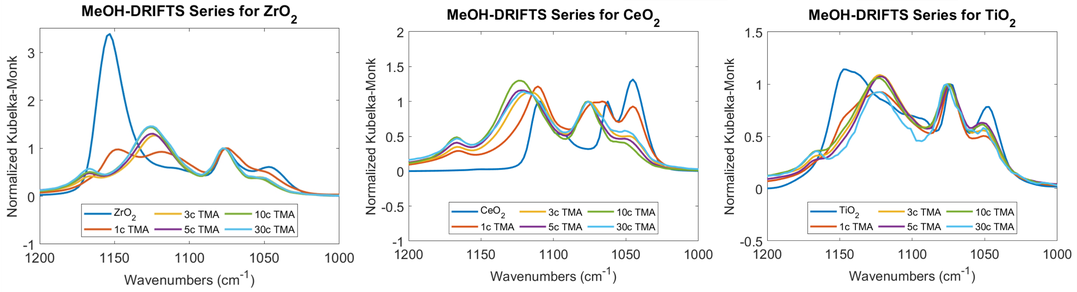
- **MeOH-DRIFTS** was used to determine the relative proportion of Lewis acid to redox sites.

*Diagram based on Huttunen, 2021. (Units: cm^{-1})



Each sample was exposed to MeOH, and the adsorption products were recorded using IR spectroscopy.

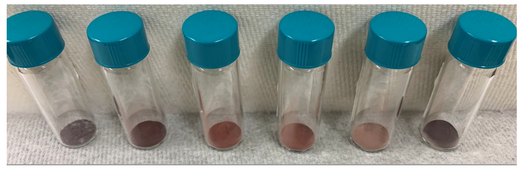


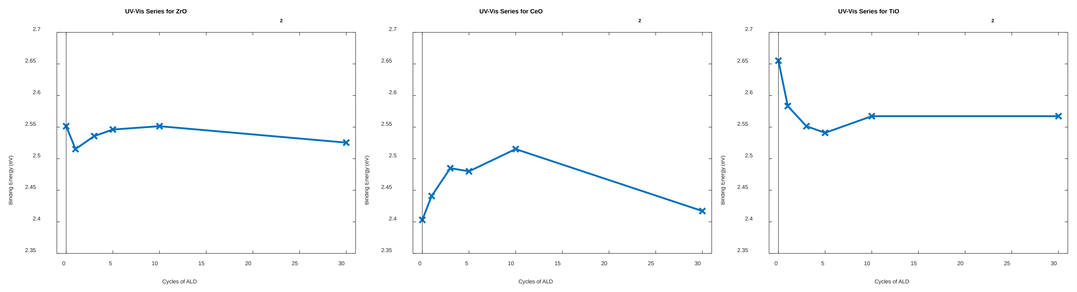


- Because the relative peak intensities of partial overcoats for CeO_2 did not fall in the expected range, the CeO_2 series indicated interfacial sites independent of the core and the overcoat of alumina.

Characterization – Alizarin Dye/UV-Vis Spectroscopy

- **Alizarin Dye/Ultraviolet-Visible Spectroscopy** was used to determine the relative Lewis acid strength.
- Alizarin dye binds to active sites on the catalyst surface. The strength of those active sites affects the electron distribution to the dye.

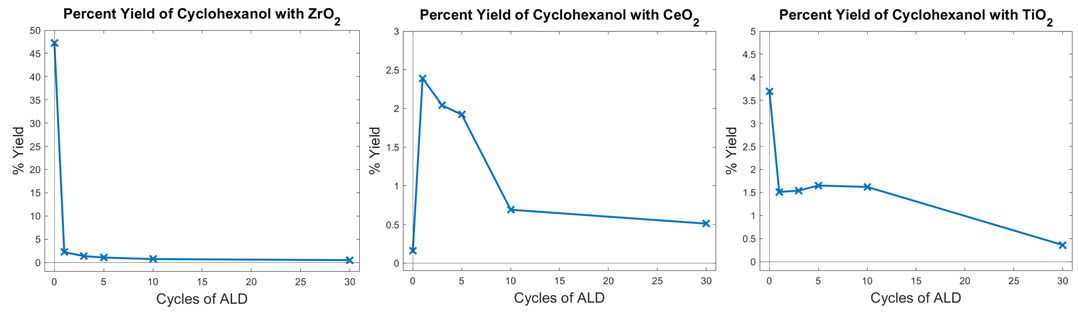




- For CeO_2, the binding energy of the intermediary overcoats (1, 3, 5, 10 cycles of ALD) were greater than the core CeO_2 or the alumina overcoat, indicating interfacial sites outside of expected behavior.

Characterization – Meerwein-Ponndorf-Verley (MPV) Reduction

- The **MPV reduction reaction** was used to probe the relative number of redox sites.



- For CeO_2 and TiO_2, there is an increase in reaction yield independent of the core or overcoat for the intermediary overcoats, indicating interfacial sites outside of expected behavior.

Implications for Catalyst Sustainability

- This study was successful in altering the surface chemistry of three metal oxide materials and determining whether they displayed interfacial sites when partially overcoated with alumina.
- This study adds to the repository of information on metal oxides and their behavior when overcoated with other materials.
- In the future, this method could be used to tailor catalysts for specific purposes, reducing waste and decreasing energy costs.
- This method could be used to create highly efficient catalysts with specific properties or binding energies.
- The synergistic effects demonstrated by some of the catalysts could be used to increase reaction yields.
- It is important to understand how overcoating a catalyst affects durability, active site availability, and reactivity.

Future Work

- Expand this study to different types of metal oxides
- Modeling the behavior of metal oxide nanoparticles when overcoated with other metal oxides.
- Engineer highly efficient catalysts using this technique
- Determine how alterations to surface chemistry affect selectivity
- Collect data on the base sites of the catalysts
- Enhance reaction sustainability across industries

Acknowledgements and References

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1. Canlas, C. P., Lu, J., Ray, N. A., Grosso-Giordano, N. A., Lee, S., Elam, J. W., Winans, R. E., Van Duyne, R. P., Stair, P. C., & Notestein, J. M. (2012). Shape-selective sieving layers on an oxide catalyst surface. *Nature Chemistry*, *4*(12), 1030–1036. https://doi.org/10.1038/nchem.1477
2. Wang, H., & Lu, J. (2018). Atomic Layer Deposition: A Gas Phase Route to Bottom-up Precise Synthesis of Heterogeneous Catalyst. *Wuli Huaxue Xuebao/ Acta Physico - Chimica Sinica*, *34*, 1321–1333. https://doi.org/10.3866/PKU.WHXB201804201
3. Marwaha, Akshey, Amit Dhir, Sunil Kumar Mahla, and Saroj Kumar Mohapatra. *"An Overview of Solid Base Heterogeneous Catalysts for Biodiesel Production." Catalysis Reviews 60, no. 4* (October 2, 2018): 594–628. https://doi.org/10.1080/01614940.2018.1494782.
4. Cao, L., & Lu, J. (2020). Atomic-scale engineering of metal–oxide interfaces for advanced catalysis using atomic layer deposition. *Catalysis Science & Technology*, *10*(9), 2695–2710. https://doi.org/10.1039/D0CY00304B
5. Huttunen, P. K., Labadini, D., Hafiz, S. S., Gokalp, S., Wolff, E. P., Martell, S. M., & Foster, M. (2021). DRIFTS investigation of methanol oxidation on CeO2 nanoparticles. *Applied Surface Science*, *554*, 149518. https://doi.org/10.1016/j.apsusc.2021.149518.
6. Nauert, Scott L., Louisa Savereide, and Justin M. Notestein. "Role of Support Lewis Acid Strength in Copper-Oxide Catalyzed Oxidative Dehydrogenation of Cyclohexane." ACS Catalysis 8, no. 8 (August 3, 2018): 7598–7607. https://doi.org/10.1021/acscatal.8b00935.
7. Komanoya, T., Nakajima, K., Kitano, M., & Hara, M. (2015). Synergistic Catalysis by Lewis Acid and Base Sites on ZrO_2 for Meerwein–Ponndorf–Verley Reduction. *The Journal of Physical Chemistry C*, *119*(47), 26540–26546. https://doi.org/10.1021/acs.jpcc.5b08355
8. Cohen, R., Graves, C. R., Nguyen, S. T., Martin, J. M. L., & Ratner, M. A. (2004). The Mechanism of Aluminum-Catalyzed Meerwein–Schmidt–Ponndorf–Verley Reduction of Carbonyls to Alcohols. *Journal of the American Chemical Society*, *126*(45), 14796–14803. https://doi.org/10.1021/ja047613m